



## Short communication

## Influence of mechanical grinding on lithium insertion and extraction properties of iron silicide/silicon composites



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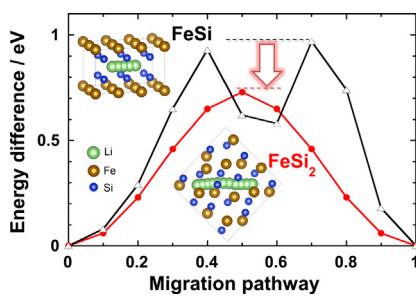
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## HIGHLIGHTS

- Anode performances of iron silicide/Si composites were studied for Li-ion battery.
- We prepared the composites by mechanical grinding for mixture of ferrosilicon and Si.
- Crystal phase changed from FeSi to FeSi<sub>2</sub> with increasing mechanical grinding time.
- Better performances were obtained for electrodes of the composites of FeSi<sub>2</sub> and Si.

## GRAPHICAL ABSTRACT



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## ABSTRACT

We prepared composite electrodes of iron silicide/Si by using mechanical grinding for mixtures of ferrosilicon and Si followed by gas-deposition, and investigated their electrochemical properties as Li-ion battery anode. With increasing the mechanical grinding time, the phase transformation from FeSi to FeSi<sub>2</sub> took place more significantly, and the composite electrode showed better cycle stabilities. There was no remarkable difference in mechanical properties and electronic conductivity between FeSi and FeSi<sub>2</sub>. On the other hand, the FeSi<sub>2</sub> electrode exhibited about three times larger capacities in comparison with the FeSi electrode. In addition, a result of our first principle calculation indicates that Li-ion can diffuse more easily in FeSi<sub>2</sub> lattice than in FeSi lattice. It is suggested that the better cyclability of the composite electrodes was attributed to the moderate reactivity of FeSi<sub>2</sub> with Li and the smooth Li-ion diffusion in it.

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## 1. Introduction

Li-ion battery has been extensively studied in these days not only for portable electronic devices but also for electric vehicles. In

particular, much larger energy density is required for the electric vehicles. Based on this requirement, Si has attracted much attention as a high-capacity anode material in the next-generation Li-ion battery. It can accommodate 3.75 Li-ions per Si atom at room temperature [1–5]. This accommodation leads to a theoretical capacity of about 3580 mA h g<sup>-1</sup>, which is approximately ten times higher than the theoretical capacity of a graphite anode in practical use. On the other hand, Si has critical disadvantages of a low

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electronic conductivity, a slow kinetics of Li-ion diffusion, and significant volume changes during Li-insertion and Li-extraction. The volume changes are a very serious problem as anode material because those cause a huge mechanical stress and a loss of electrical contact between active material and current collector. The electrode performance, consequently, drastically degrades with increasing charge–discharge cycles. Many researchers have studied various composite electrodes consisted of elemental Si and other active materials compensating for the silicon's disadvantages.

Since about 2003, the authors have intensively investigated various anode materials of intermetallic compounds [6–9], Si-based composites [10–20], and elemental Si [21–23]. As a part of these results, it has been revealed that silicon's high capacity can be effectively exerted for a long term charge–discharge cycle by a combination of elemental Si and suitable other active materials. We have reported that four kinds of properties are mainly required for the active materials as follows [10–20]:

1. Mechanical properties suitable for relaxation of the stress from Si
2. High electronic conductivity
3. Moderate reactivity with  $\text{Li}^+$
4. High thermodynamic stability

As for the fourth factor, transition metal silicides are promising as the active materials because they have generally high thermodynamic stabilities. The authors have succeeded in improving anode performances of composite electrodes consisted of elemental Si and rare-earth metal silicides such as  $\text{LaSi}_2/\text{Si}$  [11], mischmetal silicide ( $\text{MmSi}_2/\text{Si}$ ) [15], and  $\text{Gd–Si/Si}$  [25]. On the other hand, we have investigated Li-insertion/extraction properties for composite electrodes of Si and base metal silicide such as  $\text{FeSi}_2/\text{Si}$  [15,24],  $\text{NiSi}_2/\text{Si}$  [24], and  $\text{VSi}_2/\text{Si}$  [15,24]. From the viewpoint of abundance and cost, it is very important to utilize iron silicides for an electrode material of large size Li-ion battery for electric vehicles and stationary batteries.

Ferrosilicon ( $\text{Fe–Si}$ ) is one of several ferroalloys used for desulfurization and deoxidation from molten steel in a steel process. The  $\text{Fe–Si}$  is less expensive than metal grade Si (4 N purity) because it is widely used in great quantities in steel industry. It consists of mostly  $\text{FeSi}_2$  which shows charge–discharge capacities of about several  $10 \text{ mA h g}^{-1}$ . The capacities are considered an appropriate reactivity with  $\text{Li}^+$  as the third factor. Moreover,  $\text{FeSi}_2$  has a more ductile property, a higher electrical conductivity, and a higher thermodynamic stability compared with elemental Si. As a preceding study, Ai et al. reported that  $\text{FeSi}_2/\text{Si/C}$  nanocomposites were synthesized by a ball-milling method, and that the nanocomposite electrodes showed an excellent capacity retention of 92% at the 200th charge–discharge cycle in a conventional organic electrolyte [26]. On the other hand, Choi and Kim et al. prepared a sputtered  $\text{FeSi}_{2.7}$  ( $\text{FeSi}_2/\text{Si}$  composite) thin-film delivering a good retention of 92% at the 100th cycle even in an ionic liquid electrolyte [27]. They have purchased, however, commercial source materials of Fe and Si for the  $\text{FeSi}_2$  synthesis though the composites of  $\text{FeSi}_2$  and Si were found to be excellent anode active materials. Therefore, it is expected that  $\text{Fe–Si}$  becomes a promising candidate to be combined with Si as a low-cost anode material. In this study, we applied  $\text{Fe–Si}$  to Si-based composite electrodes and investigated their electrochemical properties as Li-ion battery anode.

## 2. Experimental

As an active material,  $\text{Fe–Si}$  and Si powders (Silgrain® e-Si, Elkem AS) were used. The average particle sizes of the  $\text{Fe–Si}$  and Si powders were approximately 60  $\mu\text{m}$  and 10  $\mu\text{m}$ , respectively. A

mechanical grinding (MG) was performed for a mixture of the  $\text{Fe–Si}$  and Si powders to obtain a composite active material of  $\text{Fe–Si}$  and Si ( $\text{Fe–Si/Si}$ ). The mixture of the  $\text{Fe–Si}$  and Si powders was put in a zirconia vessel together with balls so that the weight ratios of  $\text{Fe–Si:Si}$  were 70:30, 50:50, and 30:70. The weight ratio of the balls to the active materials was 15:1. The vessel used was sealed to keep an atmosphere of dry argon gas. The MG was carried out by using a high-energy planetary ball mill (P-6, Fritsch) for 10, 20, and 30 h with a rotation speed of 380 rpm at room temperature, resulting in a formation of  $\text{Fe–Si/Si}$  composite powders. The particle sizes of the composite powders were measured by a using a laser diffraction particle size analyzer (SALD-2300, Shimadzu Co. Ltd.). The typical sizes of primary particles were confirmed to be about 0.1  $\mu\text{m}$ . The crystal structure of the powders was confirmed by using X-ray diffraction (XRD, Ultima IV, Rigaku). A reference breaking strength of the powders was measured by a uniaxial compression test using a dynamic ultra-micro hardness tester (DUH-211S, Shimadzu Co. Ltd.). In this study, the reference breaking strength was defined as an applied pressure when a compressed particle of the powder showed 10% deformation compared with its original size. The electrical resistivity was measured for the powders under a uniaxial press of 55 MPa using a two probes method.

Thick-film electrodes of  $\text{Fe–Si/Si}$  composites were prepared by a gas-deposition (GD) method [9,23]. This method is a unique process in which thick-films thicker than 1  $\mu\text{m}$  consisting of various metal, alloy, and oxide powders can be easily formed by a single deposition without any binder. Procedures and conditions of thick-film electrode preparation have been described in our previous reports [9–23]. In this study, we prepared  $\text{Fe–Si/Si}$  composite film electrodes by using a nozzle with 0.5 mm in diameter, an Ar carrier gas with a purity of 99.99% under a differential pressure of  $7.0 \times 10^5 \text{ Pa}$ , and a current collector of Cu foil substrate with 20  $\mu\text{m}$  in thickness. The active material weights in the electrodes were typically kept within the range of 46–79  $\mu\text{g}$ .

Li-insertion/extraction properties of the composite electrodes were evaluated in a beaker-type three-electrode cell. We assembled the composite electrodes as a working electrode, Li metal sheets (Rare Metallic, 99.90%) as counter and reference electrodes, and  $\text{LiClO}_4$  dissolved in propylene carbonate (PC;  $\text{C}_4\text{H}_6\text{O}_3$ , Kishida Chemical Co., Ltd.) at a concentration of 1 M as the electrolyte. Galvanostatic charge–discharge tests were carried out using an electrochemical measurement system (HJ-1001 SM8A, Hokuto Denko Co., Ltd.) at 303 K with potential ranges of 0.005–2.000 V vs.  $\text{Li}/\text{Li}^+$ . The current densities were set to be  $1.0 \text{ A g}^{-1}$ , corresponding to current rates of 0.40–0.93 C.

To investigate behavior of Li-ion migration in iron silicides, we performed first principle calculations based on density functional theory (DFT) using projector augmented wave (PAW) method as implemented in the Vienna Ab Initio Simulation Package (VASP) [28,29]. The local density approximation (LDA) was also used as the term exchange correlation with a cutoff energy of 350 eV and all calculations performed nonmagnetically. The Brillouin zone sampling was done via a  $(6 \times 6 \times 6)$   $k$ -point mesh within Gamma point centered mesh scheme. Structural relaxation was carried out to determine all atomic positions after Li was inserted into crystal lattices of  $\text{FeSi}_2$  and  $\text{FeSi}$ . We calculated a formation energy  $E_f$  for Li-inserted  $\text{FeSi}_2$  in a super cell consisted of six unit cells as an interstitial solid solution ( $\text{Li}_{0.17}\text{FeSi}_2$ ) from a total energy  $E_{\text{total}}$ . The  $E_f$  of  $\text{Li}_{0.17}\text{FeSi}_2$  was defined by

$$E_f(\text{Li}_{0.17}\text{FeSi}_2) = E_{\text{total}}(\text{Li}_{0.17}\text{FeSi}_2) - 0.17E_{\text{total}}(\text{Li}) - E_{\text{total}}(\text{FeSi}_2).$$

As for Li-inserted  $\text{FeSi}$ ,  $E_f$  of  $\text{Li}_{0.06}\text{FeSi}$  in a super cell consisted of four unit cells was calculated by equation of

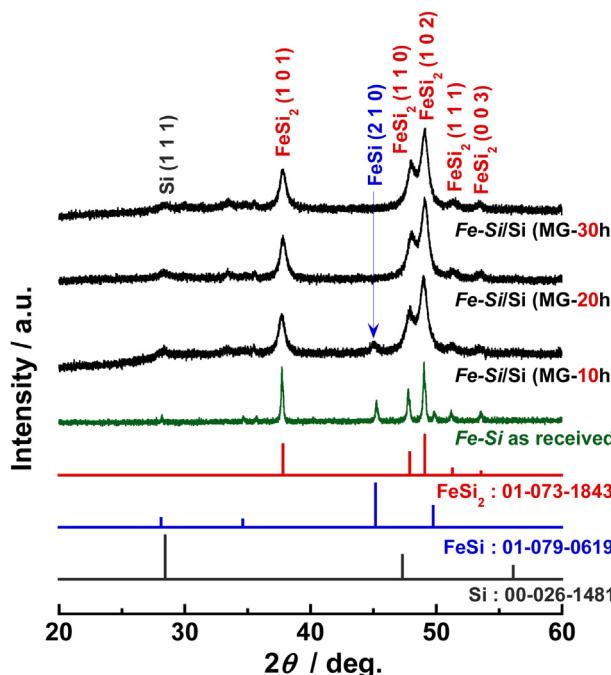


Fig. 1. XRD patterns of  $Fe-Si/Si$  composite powders prepared by MG with different grinding times.

$$E_f(Li_{0.06}FeSi) = E_{\text{total}}(Li_{0.06}FeSi) - 0.06E_{\text{total}}(Li) - E_{\text{total}}(FeSi).$$

To evaluate Li migration in crystal structure, we calculated the formation energies in migration pathway between the most stable interstitial sites of Li. As an energy barrier for the migration, changes in formation energies of Li-inserted  $FeSi_2$  were investigated when Li migrates between adjacent stable sites.

### 3. Results and discussion

Fig. 1 shows XRD patterns of  $Fe-Si$  powder as received. We can recognize diffraction peaks of not only  $FeSi_2$  (Inorganic Crystal Structure Database, ICSD No.01-073-1843) but also  $FeSi$  (ICSD No.01-079-0619). It was confirmed that  $Fe-Si$  powder consists of a

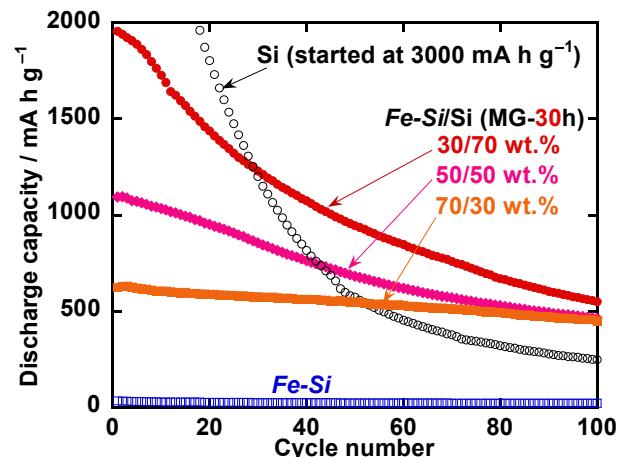


Fig. 3. Charge–discharge cycling performances of the  $Fe-Si/Si$  composite electrodes. For comparison, this figure shows results for electrodes of Si alone and  $Fe-Si$  alone.

mixture of  $FeSi_2$  and  $FeSi$ . A thick-film electrode using  $Fe-Si$  alone, prepared for a preliminary experiment, showed low discharge capacities less than  $20 \text{ mA h g}^{-1}$  and a very stable cyclability as we expected. Although as-received  $Fe-Si$  alone is not suitable for anode material, we expected high capacity and stable cyclability by compounding  $Fe-Si$  with elemental Si using MG. Fig. 1 compares XRD patterns of  $Fe-Si/Si$  composite powders prepared by MG for 10–30 h. In each composite powder,  $FeSi_2$  and Si peaks were observed. On the other hand, the peak intensity of  $FeSi$  was decreased with increasing MG time, and the peak disappeared when MG time reached 20 h. This indicates that a phase transformation from  $FeSi$  to  $FeSi_2$  took place by MG with the existence of excess Si. These results suggest that the phase transformation to  $FeSi_2$  almost completed in case of MG 30 h (Fig. S1), and that  $FeSi_2$  and Si phases uniformly intermixed in  $Fe-Si/Si$  composites. The crystalline size of  $FeSi_2$  was estimated to be about 14 nm by using Scherrer equation.

Fig. 2 shows potential profiles at the first cycle for electrodes of  $Fe-Si/Si$  composites prepared by MG for 30 h. The weight ratios of  $Fe-Si/Si$  were 30/70, 50/50, and 70/30 wt.%. In the all electrodes, we observed potential plateaus in the charge (lithiation) reaction at 0.1–0.3 V vs.  $Li/Li^+$  and in the discharge (delithiation) reaction at

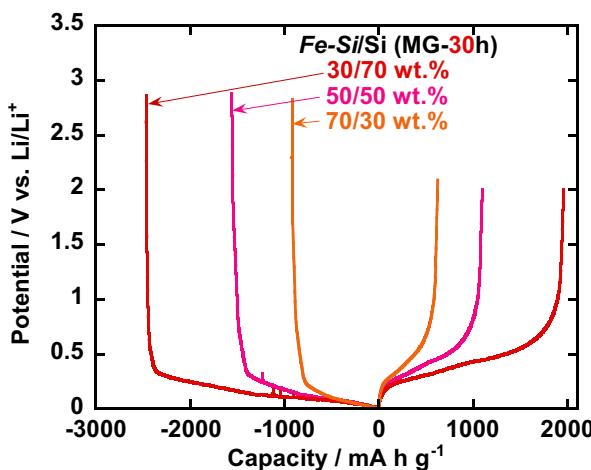


Fig. 2. Initial charge–discharge curves of thick-film electrodes using  $Fe-Si/Si$  composites prepared by MG for 30 h. The weight ratios of  $Fe-Si/Si$  were 30/70, 50/50, and 70/30 wt.%.

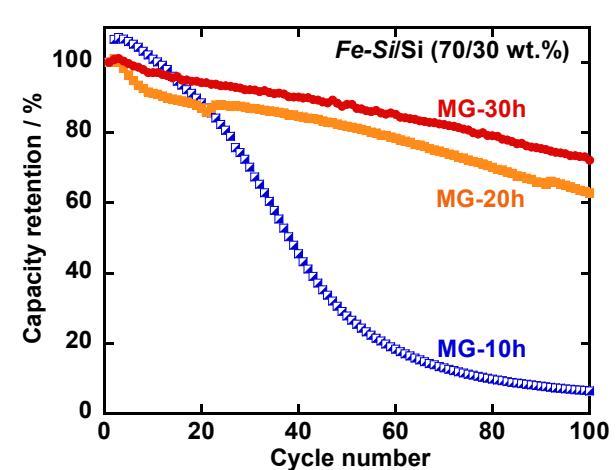
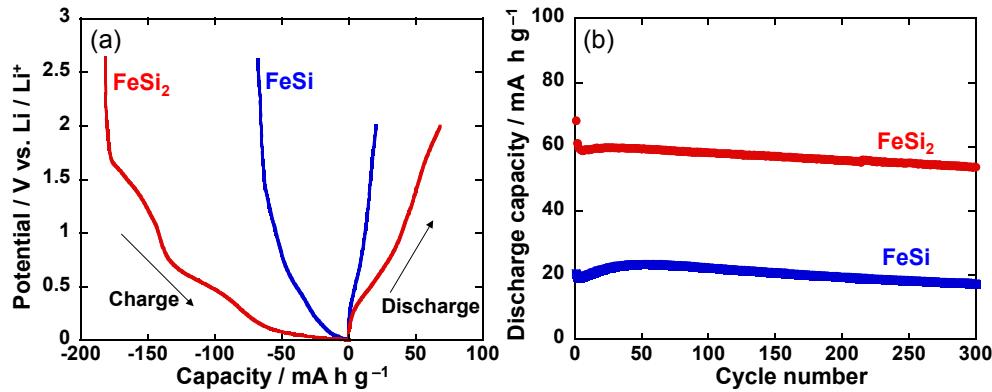


Fig. 4. Effect of MG time on capacity retention of  $Fe-Si/Si$  composite electrodes with weight ratio of 70/30 wt.%. In cases of MG times of 10, 20, and 30 h, the electrodes showed initial capacities of 750, 600, and  $620 \text{ mA h g}^{-1}$ .



**Fig. 5.** (a) Charge–discharge curves and (b) cycle stability for electrode of FeSi<sub>2</sub> alone prepared by mechanical alloying method. For comparison, anode properties of FeSi electrode were also shown in the figure.

0.3–0.5 V vs. Li/Li<sup>+</sup>, indicating alloying and dealloying reactions of Li–Si.

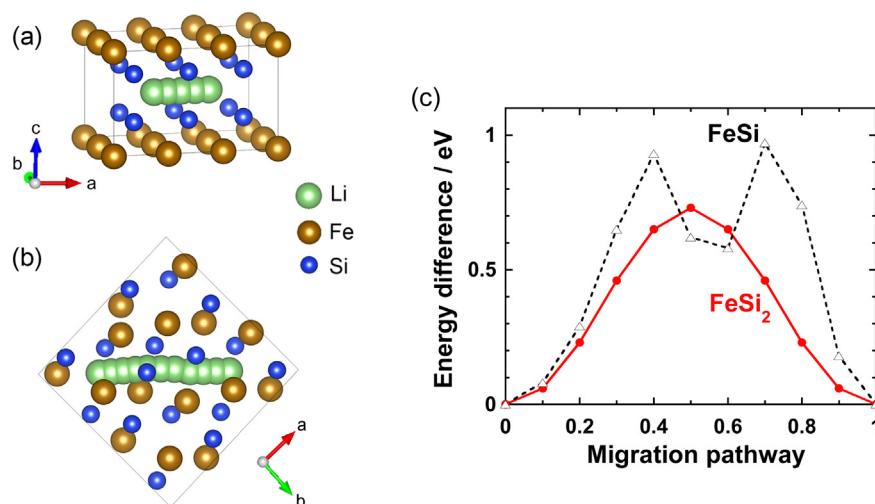
Fig. 3 represents cycling performances of the Fe–Si/Si composite electrodes as compared with those of electrodes using Si alone and Fe–Si alone. The discharge capacity of the Si electrode rapidly decreased with increasing the cycle number. This poor cyclability originates in properties of Si itself: low electronic conductivity, slow kinetics of Li-ion diffusion, and significant volume changes during Li-insertion and Li-extraction. In particular, the volume changes cause pulverization and loss of electrical contact for active material layer, resulting in the significant capacity fading. On the other hand, the capacity fading was suppressed for the Fe–Si/Si composite electrodes. After 30–50 cycles, the capacity of the composite electrodes exceeded that of the Si electrode. This result demonstrated that compounding Fe–Si and Si is effective for improving performance of Si-based anode. It is easily suggested that FeSi<sub>2</sub> phase in the composite can improve electrical conductivity and can relax the stress from Si. With increasing the amount of Fe–Si in the composite, the cyclability was much improved though the initial capacity was reduced owing to lower amount of elemental Si in it.

To discuss the effect of MG treatment on the good cyclability, we focused on the time of MG treatment. Fig. 4 presents relationship between cycle number and retention of initial capacity for the

Fe–Si/Si electrodes with the ratio of 70/30 wt.%, and dependence of MG time on the retention. In case of MG for 10 h, the electrode showed a drastic retention decay by the 60th cycle and a very low retention of 7% at the 100th cycle. In contrast, when MG time was 20 h or more, the electrodes exhibited good retentions higher than 60% for 100 cycles. We considered that this improved retention should be correlated with the phase transformation from FeSi to FeSi<sub>2</sub> by MG.

As we mentioned in the introduction section, active material combining with Si in composite electrode is required to have four kinds of important properties: (i) mechanical properties suitable for relaxation of the stress from Si, (ii) high electronic conductivity, (iii) moderate reactivity with Li<sup>+</sup>, and (iv) high thermodynamic stability. To make clear difference in these properties between FeSi and FeSi<sub>2</sub>, we separately prepared single phase FeSi and FeSi<sub>2</sub> powders by a mechanical alloying method [11,15,19].

By a uniaxial compression test using a dynamic ultra-micro hardness tester, we evaluated a reference breaking strength (pressure required for 10% deformation) [15] for FeSi and FeSi<sub>2</sub> powders. The breaking strengths of FeSi and FeSi<sub>2</sub> were 229 ± 21 and 213 ± 44 MPa, which were much lower than the value of 409 ± 68 MPa obtained for Si. This result revealed that both silicides have a favorable mechanical property to relax the stress from Si. No remarkable difference in the mechanical property was observed



**Fig. 6.** Migration pathway between the most stable interstitial sites for Li in crystal structures of (a) FeSi<sub>2</sub> and (b) FeSi. The figures were created using VESTA package [32]. (c) Change in formation energies of Li<sub>x</sub>FeSi<sub>2</sub> when Li migrates between adjacent stable sites. The formation energy at the most stable site of Li was set to be 0.

between FeSi and FeSi<sub>2</sub>. An electrical conductivity was studied under a uniaxial pressure for active material powder by using our measurement system [15]. The resistivity of both silicides was  $2.6 \times 10^1 \Omega \text{ cm}$ , which was about 100 times lower than that of  $6.0 \times 10^3 \Omega \text{ cm}$  in case of Si. It was found that FeSi and FeSi<sub>2</sub> equally improve the electrical conductivity of the composite electrodes. As for thermodynamic stability, Acker et al. have reported that the standard enthalpies of formation of FeSi and FeSi<sub>2</sub> were  $-74$  and  $-79 \text{ kJ mol}^{-1}$  [30]. Thus, FeSi has as good a thermodynamic stability as FeSi<sub>2</sub> does. There was no significant difference in the three properties, thereby indicating that an electrochemical reactivity of silicides with Li<sup>+</sup> should be different.

Fig. 5 shows Li-insertion/extraction properties of thick-film electrodes using FeSi and FeSi<sub>2</sub> prepared by the mechanical alloying method. In each electrode, gentle potential shoulders were observed in the initial charge–discharge curves (Fig. 5(a)). We consider that these silicides reversibly store Li-ions at interstitial sites in their crystal lattice as Mg<sub>2</sub>Ge does [31] though detailed reaction mechanism is still unclear. Both electrodes showed very stable cyclability for 300 cycles. The discharge capacities of the FeSi<sub>2</sub> electrode were three times larger than those of the FeSi electrode. As for metal silicide-based composite electrodes, it is suggested that a discharge capacity of about several  $10 \text{ mA h g}^{-1}$  for silicide electrodes is favorable for improving cyclability of composite electrodes though it depends on the kind of active materials and conditions of charge–discharge tests. In a typical condition of our experiments, when electrodes of metal silicide alone showed reversible capacities of about several  $10 \text{ mA h g}^{-1}$ , silicide/Si composite electrodes exhibited better cycling performances [11,15,25]. In contrast, a NiSi<sub>2</sub> electrode showed higher initial capacity than  $100 \text{ mA h g}^{-1}$ , and thus poor cycle stability was obtained for a NiSi<sub>2</sub>/Si composite electrode because the higher reactivity of NiSi<sub>2</sub> with Li leads to its large volume change and disintegration of the composite electrode [24].

Fig. 6(a) and (b) illustrate migration pathway between the most stable interstitial sites for Li in the structures of (a) tetragonal FeSi<sub>2</sub> and (b) cubic FeSi. The figures were created using VESTA package by K. Momma and F. Izumi [32]. The migrations in FeSi<sub>2</sub> and FeSi were calculated along [100] and [110] directions in which Li has the longest interatomic distances to nearest neighbor atoms of Si and Fe. In case of FeSi, we calculated the formation energies in curved pathway with consideration for asymmetry of atomic configuration. As we expected, FeSi<sub>2</sub> exhibited less energy barrier for Li migration in the pathway than FeSi (Fig. 6(c)) though Li concentration in the cell of Li<sub>0.17</sub>FeSi<sub>2</sub> is higher than that of Li<sub>0.06</sub>FeSi. This calculation results indicate that FeSi<sub>2</sub> has a more favorable structure for Li migration than FeSi. Taking account of the larger reversible capacities of the FeSi<sub>2</sub> electrode as shown in Fig. 5(b), FeSi<sub>2</sub> phase has an advantage not only in smooth Li-ion diffusion but also in the quantity of Li-insertion/extraction. Therefore, we consider that the electrode of Fe–Si/Si composite, in which FeSi transformed to FeSi<sub>2</sub> by MG, showed the good cyclability.

#### 4. Conclusions

We prepared the Fe–Si/Si composite by using MG for elemental Si and ferrosilicon, which is industrially available and less expensive material, and investigated the influence of MG on the anode performance of the composites. With increasing the MG time, the phase transformation from FeSi to FeSi<sub>2</sub> took place more significantly, and the composite electrodes exhibited higher capacity retention for 100 cycles. As a result of measurements for the

mechanical properties and the electronic conductivity, there was no remarkable difference in these properties between FeSi and FeSi<sub>2</sub>. On the other hand, the FeSi<sub>2</sub> exhibited about three times larger capacities in comparison with the FeSi electrode. In addition, a result of our first principle calculation indicates that Li-ion can diffuse more easily in FeSi<sub>2</sub> lattice than FeSi lattice. We consider that the better cyclability of the composite electrodes was attributed to the moderate reactivity of FeSi<sub>2</sub> with Li and the smooth Li-ion diffusion in it.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.06.105>.

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